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(54) A method of printing a substrate.

(57) The invention relates to a method of printing a substrate in a pattern with a viscous mass in the form of a foam using a screen printing machine.

In order to provide new structures, especially in combination with the printing of fibrous webs, the invention is characterized in that the foam used has meta-stable foam properties. Meta-stable means that no liquid is settled after 24 hours standing at 20 °C.

EP 0 184 596 A1

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A method of printing a substrate.

This invention relates to a method of printing a substrate in a pattern with a viscous mass in the form of a foam using a screen printing machine.

A similar method is disclosed in the published European patent application 47 559. The disclosure thereof is incorporated herein by reference. In that application, the use of a foam is mentioned at the end.

Experience with foams hitherto used for this purpose has taught that the pattern printed into the substrate loses the foamed form virtually immediately. The foam bubbles burst before or during drying, and the result is that the material fully comes into direct contact with the substrate. In addition there may be a slight degree of migration.

In the patent application referred to, the use of highly stable foams is explicitly avoided, because they would not be absorbed by the substrate fast enough. For such fast absorption, a lower foam stability is considered essential.

Surprisingly it has now been found that, with the squeegee device described in EP-A 47 559, in particular for printing fibrous webs, the use of highly stable foams is quite possible and even may involve a number of technical advantages.

The invention is accordingly characterized by using a foam having meta-stable foam properties. Preferably, the starting point is such a stable foam that the foam structure is substantially maintained during the application in the substrate and during the subsequent drying.

As, during the application of the foam to, or in, the substrate, and during the subsequent transport of the treated substrate, the foam will inevitably be subjected to high shearing forces, a small proportion of the foam cells will loose their original structure and burst. This will generally not be in excess of 10-15% of the cells.

In the case of fibrous webs, one factor is the certain depth to which the foam pressed from the rotation screen can penetrate inwardly. When the foam stability is so high that during

and after the passage of the screen the shear forces do not result in unduly high destruction of the external foam structure, a screen print in the form of foam is locally left in the substrate. Surprisingly it has been found that, with sufficiently stable foam, it is possible to print with very sharp contours in this manner and that after drying the original foam form can be maintained. While maintaining the advantages that can be gained by printing with foam on the rotation-screen printing machine, such as accurate dosage per unit area, economic power consumption, and the possibility of fast switching in production batches, this effect additionally gives the advantages directly related to the external foam form of the printing material. This is best seen when the fibrous web is printed with a binder composition brought into the suitable foam form. It can then be seen that not only the location, but the depth of penetration of the printed foam composition can be accurately controlled.

When ejected from the screen, the foam is clearly deposited in the fleece material as an extrusion pillar. By means of this control of the foam/ distribution all sorts of material effects can be achieved in the final product; not only in decorative respect, but also structurally. This opens up the constructive route to new types of fibrous webs. In these structures, the desired combination of properties can be supported by a suitable material selection of binder type, fiber mixture and web structure. The technique of pattern printing by means of dimensionally stable foam compositions opens up the possibility of introducing new structures by:

a. depositing a sharply defined pattern in the plane of the web. This has a decorative significance, but especially in the case of fibrous webs, also one of surface structure. The binder pattern thus produces a highly flexible web with a limited number of free fibers at the surface.

b. operating with internal binder-free zones, as viewed cross-sectionally of the web, by controlling the depth of penetration of the foam paste. This can be of importance for controlling

the absorptive power.

c. using this printing technique by adjustment of the squeegee-screen system for applying a relief pattern of dimensionally stable foam.

d. realizing two-fold or multi-fold printings on one or both sides of the web before effecting the aftertreatment in the dryer, common to all prints.

All this is demonstrated in the examples, without all possibilities being exhaustively dealt with therein.

These examples also show that, when using dimensionally stable foam paste by means of the screen printing technique only, is it possible to have two or more printing treatments take place synchronously or one immediately after another, and only then followed by drying. The advantage of this treatment as far as process economy is concerned, is evident. Of course, in at least one of these printings the meta-stable foam of the invention should be used.

Synchronously printing a flexible, porous, flat structure, such as a fibrous web, with pastes on opposite sides is described in the published European patent application No. 54628. In it, however, it is on the one hand explicitly argued that the two sides should be treated with a different printing technique, and, on the other hand, no use is made of a meta-stable, high-stability foam at all. It is the very combination of, on the one hand, the method improved with highly stable foam when using the rotary-screen machine according to EP-A 47 559 with, on the other hand, the possibility of applying a plurality of printing treatments at the same time or in series, which possibility has arisen as a result of the highly stable foam, that the subsequent heat drying treatment can take place for all printing treatments at the same time.

The composition of the dimensionally stable foam does not involve any novel particular aspects: the high foam stability can be achieved by using features long since known to the art. Thus, in addition to a suitable surfactant, one may provide for a high viscosity, for the addition of foam stabilizers or anti-desiccants, for the use of low-molecular emulsifiers, and for the use of a high

dry content. The dry content should be at least 20%. The higher the content of dry matter, the faster the binder will coagulate upon forced drying, as a result of which the foam structure is maintained.

The composition of matter from which the foam is prepared usually comprises an aqueous dispersion, although it is quite possible to use other solvents or dispersing agents, such as ethylacetate. Advantageously, water is used as this presents little or no environmental problems.

If the binder itself is liquid as can be the case with e.g. epoxy- systems or liquidized, reactive waterfree systems, it is also possible to dispense with the solvent.

Of importance to the dimensionally meta-stable foam, in addition to the composition, is the physical fineness. For the stability it is of importance that the average diameter of the foam bubbles should be less than half the average fiber interspace in the web. The suitability of the foam for the printing process on the rotation-screen machine can be evaluated in various ways. Thus, for example, use can be made of a laboratory high-speed mixer to beat foam to a certain fineness to be expressed in the density in g/l. The higher the density, the coarser the foam bubbles are. The advantageously used values range between 50 and 300 g/l.

The term "meta-stable" foam as used in this connection means a foam which satisfies the following test.

A volume of 1 l of foam is separated in a measuring cylinder covered, and allowed to stand at 20°C for 24 hours. Evaluation is then effected by measuring the amount of liquid settled. A foam suitable for use in the dimensionally stable foam paste will exhibit no settled liquid after 24 hours. Such a foam is considered meta-stable.

According to the invention, it is possible to print various substrates. Suitable are, for example, all sorts of textile fabrics, knitted fabrics, for example, a "Raschel" fabric or a tricot fabric, "non-wovens" whether or not in combination with a fabric scrim, foam structures, for example coarse polyurethane foam, and the like.

More in particular it is possible to use a slightly reinforced web such as combined structure of a fibrous web with a network, a woven fabric or a knitted fabric.

Another alternative which can be advantageous is the use of a substrate in the form of a textile structure or a foam structure.

Suitable textile fabrics are cotton and woollen fabrics, and suitable "non-wovens" are especially fibrous webs made from natural fibers, and fibers of synthetic plastics material, but also fibers of glass, carbon and asbestos.

Printing can be effected with all sorts of substances, depending on the final product contemplated. It is not necessary for printing to be effected in a design. It is possible to print the entire surface. Some examples of applications are the binding of a fibrous web, printing a fibrous web in a pattern with a decorative character, decoratively binding a needled web, rendering a substrate water-repellent, or, on the other hand, applying a water-absorbing layer.

The meta-stable foam is prepared starting from known components. Generally speaking, the composition from which the foam is made contains water, a binder, a thickener, a surfactant (wetting agent), a foam stabilizer and possibly a filler. Depending on the final product contemplated, the composition contains one or more other substances to be applied to the substrate. These may be, for example, pigments, water-proofing compounds, compounds providing water absorbency, binders, antioxidants, functional compounds such as carbon black, and the like.

Binders suitable for use in the present invention are lower alkylacrylates, styrene-butadiene rubber, acrylonitrile rubber, polyurethane, epoxy-resins, polyvinylchloride, polyvinylidene-chloride and copolymers of vinylidene chloride with other monomers, polyvinylacetate, partially hydrolyzed polyvinylacetate, polyvinyl-alcohol, polyvinylpyrrolidone, and the like. Optionally these binders can be provided with acidic groups, for example by carboxylating them. A suitable carboxylating agent is for example maleic anhydride.

Suitable surfactants are of the anionic or non-ionic type, such as soaps, alkyl-aryl sulfonates, fatty alcohol sulfates , ethoxylated fatty acid compounds and the like.

As foam stabilizers suitable for use in the present invention the following compounds can be used: fatty acid-amide condensates, ammonium- and potassium stearate, cyclohexanole alkylamino salts of acetic acid, formic acid and propionic acid, tertiary amino oxides and the like.

The fillers to be used in connection with the present invention are the usual fillers for foam printing, and comprise pigments, active components such as carbon black, hydrated alumina, blown silica, etc.

The particle size of the fillers is preferably at most 20 µm, as the presence of larger particles can interfere with the process of the invention.

The foam composition is to be converted into a meta-stable foam in known manner, for example, by beating the composition in a high-speed mixer with air or another gas.

The invention is also directed to a printed substrate produced with the method of the invention. These printed substrates are novel products as set out hereinbefore.

In the following Examples I to VI, the use of meta-stable foam is illustrated. Table A specifies the properties of the foams used.

Example I

Bonding and dot-printing a web in one pass for making an adhesive interlining.

A fibrous web of 30 g/m^2, consisting of 50% 1.7 dtex, 40 mm viscose fibers, 40% 1.7 dtex, 60 mm polyester fibers and 10% polyester melting fiber having a melting point of 130^{0}C, is thermo-fixed with hot air and then printed on a rotary screen machine, by means of a patterned stencil having an open area of 25%, with a quantity of 25 g/m^2 meta-stable foam on the basis of a latex of carboxylated butylacrylate resin having a dry content of 40% and a foam density of 200 g/l. At the same time, or immediately thereafter, the web is printed on the same machine, and in register with

the preceding print pattern with dots of a latent adhesive by means of a stencil of a similar pattern but with smaller apertures, so that the open area is now 10%. The latent adhesive is a copolyamide solution in p-toluenesulfonamide having a dry content of 30%, which is applied in a quantity of 50 g/m^2.

After this double screen printing passage, the web is uniformly dried, gelled and cured for 30 seconds at 150°C.

The registered prints can be applied, as desired, on the same side of the fibrous web or on opposite sides. Rotation-screen machines equipped for this purpose are known per se.

Example II

Bonding a fibrous web in unicolour with stable foam and dot-printing with a latent adhesive.

A fibrous web of 50 g/m^2, consisting of 30% 1.7 dtex, 40 mm nylon 66 fibers, 60% 3.3 dtex, 40 mm nylon 66 fibers and 10% 1.7 dtex, 40 mm polypropylene fibers, is thermofixed and subsequently printed on a rotary screen machine with 75 g/m^2 stable foam on the basis of a latex of soft carboxylated styrene-butadiene rubber having a dry content of 20% and a foam density of 100 g/l by means of a rotation screen with a fineness of 60 mesh and an open area of 45%. Subsequently the fibrous web thus treated is dot-printed with a quantity of 30 g/m^2 of a copolyester solution provided with a foaming agent, having a dry content of 30%, by means of a rotation screen having a fineness of 17 mesh. After these two printing passages, the binder is uniformly dried and hardened in a furnace, and at the same time the printed dots of the latent copolyamide adhesive are foamed and gelled. This heat passage at 150°C takes 40 seconds. The product is suitable for use as an interlining.

Example III

Decoratively bonding of a needled web by means of pigmented foam binders.

A 1.1 mm thick needled web of 150 g/m^2, consisting of 100% 1.7 dtex, 40 mm polyester fibers, and rigidified under a light calendar pressure at 220°C, is passed along three rotary-screen stencils, whereby, successively, the following binder compositions are applied:

a. a quantity of 25 g/m^2 of an instable foam on the basis of a light-grey pigmented carboxylated acrylate latex having a dry content of 40%, exhibiting soft rubber characteristics and having a foam density of 100 g/l. Printing was effected with a regular open-screen stencil having a fineness of 60 mesh under such a pressure in the internal squeegee system that the binder penetrates 0.25 mm into the fleece.

b. by means of a patterned stencil having an open area of 60%, a quantity of 6.5 g/m^2 of a dimensionally stable foam, having a dry content of 34% on the basis of a light-grey pigmented latex of a soft crosslinkable polyurethane having a foam density of 100 g/l. This foam is caused to penetrate 0.1 mm into the fleece.

c. by means of a patterned stencil having an open area of 10%, a quantity of 2.0 g/m^2 of a dimensionally stable foam, having a dry content of 43% , on the basis of a dark-grey pigmented latex of soft crosslinkable polyurethane having a foam density of 200 g/l. This foam is caused to penetrate 0.1 mm into the fleece.

After these three passages, the product is dried in a furnace and hardened at 160°C for 2 minutes. The product can be used as a suitcase liner.

Example IV

Bonding and at the same time oil-proofing and water-proofing a non-woven structure.

A 1.0 mm thick fibrous web of 60 g/m^2, consisting of a mixture of black polyester fiber of 30% 1.7 dtex/40 mm and 60% 3.3 dtex/40 mm and 10% of glossy polyester melting fiber having a melting point of 130°C, is after thermofixation, bonded by means of a rotary screen having an entirely open, i.e. non-patterned, screen area/laden with a quantity of 100 g/m^2 of a dimensionally stable foam having a dry content of 30% on the basis of a latex of non-filled, hard, crosslinkable acrylate rubber. Foam density is 100 g/l. This first rotary-screen passage is followed by a second passage along a rotary screen that is also open, and whereby, on the same side of the web, a quantity of 10 g/m^2 of dimensionally stable foam mixture, with a dry content of 20%, on the basis of a non-filled composition of melamine-fatty acid condensate and a fluorocarbon

in the form of an emulsion. Foam density is 100 g/l. The depth of penetration of the latter passage is 0.1 mm. These two rotary-screen passages are followed, for drying and complete cross-linking by a treatment in a furnace in 130°C for 2 minutes. The product can be used for upholstery in motorcars.

Example V

Printing webbing with different foam mixtures in a pattern.

A 2.0 mm thick white polyester fibrous web consisting of a mixture of 30% 5.0 dtex/50 mm, 40% 17.0 dtex/80 mm and 30% 3.3 dtex/40 mm, with 40% of the kind last-mentioned consisting of a melting fiber having a softening range of 160-220°C is, after fixation at 220°C, printed by means of two immediately consecutive rotary screen passages.

The first screen has a pattern with 80% free apertures of the screen area. By means of this screen, a quantity of 145 g/m^2 of a dimensionally stable foam composition, having a dry content of 45%, on the basis of a latex of a hard methyl-methacrylate resin with a foam density of 100 g/l is applied.

The second screen is patterned with 20% free apertures of the screen area and prints the substrate in registry with the pattern of the first screen, namely, on the still open substrate portions. This is effected by means of a dimensionally stable foam containing 100% epoxy resin and having a foam density of 200 g/l, in a quantity of 100 g/m^2.

After the two printing passages, the product is substantially dried at 150°C for 2 minutes and then subjected to after-drying and hardening at 140°C for 1 minute.

The product obtained cannot be crushed, and can be used as a flexible spacer for lamination.

Example VI

Application of a non-corrosive water-absorbent layer to a web.

A polyester fibrous web of 40 g/m^2, consisting of 90% 1.7 dtex/40 mm and 10% 1.7 dtex melting fiber having a melting point of 130°C, and having a ratio in tensile strength in the longitudinal and transverse directions of 5:1 is provided by means

of a rotary screen with a continuous top coating of 115 g/m^2 of dimensionally stable foam on the basis of polyvinyl alcohol solution in vinylacetate, having a dry content of 40%, with 30% of the dry matter consisting of super-absorbent acrylate powder. Foam density is 150 g/l.

Immediately thereafter, in a next rotary screen pass, the same side of the web is provided with a dose of 10 g/m^2 of an instable, thickened foam, having a dry content of 10%, and a foam density of 200 g/l, on the basis of a solution of benzotriazole in ethanol. The product is dried and hardened at 50°C for 1 minute.

In the following Table A, some properties of the various foam compositions are set forth. Please note that the foam stability and the meta-stability tests are two different tests. In the first one the ratio (m%) between the original volume of the foam and the volume after the specified time is given. This test is used to evaluate meta-stable foams among each other. The last test indicates if a foam is meta-stable or not.

TABLE A

Ex. composition	pH	Visc. (cp) 10 rev/m	Visc. (cp) 100 rev/m	Dry matter wt.%	Foam stability after .... hours	meta-stability*
I butylacrylate resin latex	9	2300	560	40.0	110 g/l: 92% (96 h)	+
					200 g/l: 95% (96 h)	
II soft SBR latex	9	2500	540	20	100 g/l: 90% (96 h)	+
III a) non-stable soft carboxylated acrylate latex	9	70	50	40,0	70 g/l: 0% (24 h)	-
					100 g/l: 0% (24 h)	
III b) polyurethane binder	9	1600	900	34,0	100 g/l: 90% (96 h)	+
IV a) hard, crosslinkable acrylate latex	9	4600	1100	30,0	100 g/l: 95% (48 h)	+
					165 g/l: 95% (48 h)	
IV b) fluoro-carbon emulsion	6,2	4400	800	20,0	100 g/l: 85% (24 h)	+
V a) hard, methyl-methacrylate resin/ PVDC-dispersion	9	3600	1500	45	100 g/l: 85% (96 h)	+
					150 g/l: 90% (96 h)	+
V b) epoxy-resin binder	-	90000	14500	100	350 g/l: 80% (24 h) (pot-life appr. 8 h)	+

*)
+ satisfies the test for meta-stability
- does not satisfy the test for meta-stability.

In Table B, the composition of the various printing compositions is given. In the column headed "amount" the amount of product (emulsion, powder etc.) is given, inclusive of solvent etc. In the last column, the composition is given in % with respect to the total amount of dry matter.

TABLE B

Ex.	type	composition compound	amount (wt. parts)	% dry content
I	butylacrylate resin latex	- soft carboxylated butyl-acrylate polymer dispersion	1000	94,6
		- NH_4Cl solution	15	0,3
		- acrylic acid thickener	15	0,9
		- ammonium stearate dispersion	60	3,6
		- 2-amino-2-hydroxyethylpropane	3	0,6
		- water	145	-
IIa	SBR-foam binder	- soft carboxylated SBR copolymer dispersion	970	79,4
		- 3-methoxy-methylmelamine	56	9,5
		- HCl-salt of 2-amino-2-hydroxy-methylpropane	13	0,8
		- acrylic acid thickener	60	3,6
		- 2-amino-2-hydroxymethylpropane	4	0,6
		- ammonium stearate	60	3,6
		- green pigment-dispersion	25	2,5
		- water	1300	-

0184596

TABLE B (continued)

Ex.	type	composition compound	amount (wt. parts)	% dry content
IIb	adhesive composition (30.0% dry matter)	- copolyester powder	400	96,4
		- stabiliser	4	1,0
		- acrylate thickener	24	2,0
		- TiO_2 dispersion	4	0,5
		- optical whitener	1	0,1
		- water	1000	-
IIIa	acrylate-foam binder	- soft carboxylated acrylate resin dispersion	475	43,4
		- dimethoxy methyl dihydroxy-ethylene ureum	12	1,1
		- trimethoxy methyl melamine	13,5	2,5
		- hard carboxylated metha-crylate dispersion	526	52,6
		- acrylic acid thickener	5	0,3
		- carbon black pigment	1,5	0,1
		- stabilizer	1	0,2
		- water	216	-

0184596

TABLE B (continued)

Ex.	type	composition compound	amount (wt. parts)	% dry content
IIIb	polyurethane binder	- soft, crosslinkable polyurethane dispersion	1395	92,5
		- aziridine complex	15	3,0
		- acrylic acid thickener	8	0,5
		- carbon black pigment	5	0,3
		- 2-amino-2-hydroxymethyl propane	0,5	0,1
		- ammonium stearate	60	3,6
IVa	acrylate-based binder	- hard, crosslinkable acrylate copolymer dispersion	947	89,1
		- phosphoric acid thickener	400	7,5
		- ammonia	6	0,1
		- ammoniumstearate	60	3,3
		- water	621	-
IVb	fluoro-carbon based emulsion	- fluorocarbon emulsion	542	20,5
		- melamine-fatty acid condensate	469	9,5
		- amphoteric foam stabilizer	13	1,6
		- soft acrylate binder	1080	62,6
		- polyphosphate thickener	50	5,8
		- water	1720	-

TABLE B (continued)

Ex.	type	composition compound	amount (wt. parts)	% dry content
Va	methyl-methacrylate based binder	- hard acrylate polymer dispersion	500	37,2
		- polymeric filler based upon PVDC	500	52,2
		- wetting agent based upon poly-amino-amide	150	5,6
		- acrylic acid thickener	30	1,3
		- acetic acid salt of fatty-amine complex	19	2,8
		- dimethyl-ethanolamine	5	0,7
		- TiO_2 dispersion	3	0,2
		- water	250	-

TABLE B (continued)

Ex.	type	composition compound	amount (wt. parts)	% dry content
Vb	epoxy resin based binder	- epoxy resin (bisphenol F)	1000	37,4
		- curing agent (isophoron complex)	550	20,6
		- foam stabilizer	45	1,7
		- plasticizer	75	2,9
		- aluminium-trihydrate (1-2 µm)	1000	37,4

CLAIMS

1. A method of printing a substrate in a pattern with a viscous mass in the form of a foam, using a screen printing machine, characterized by using a foam having meta-stable foam properties.

2. A method according to claim 1, characterized in that the structure of the foam and the pattern of the stencil are substantially maintained during transfer into the substrate and during subsequent drying.

3. A method according to claim 1, characterized in that the substrate is a slightly reinforced fibrous web.

4. A method according to claim 1, characterized by applying such a pressure within the squeegee system of the screen printing machine that, when transferred to the substrate, the foam composition can penetrate the substrate to a desired adjustable depth while maintaining its foam structure.

5. A method according to claim 1, characterized in that the same substrate is printed at least two times, using rotating stencils before subjecting the substrate thus printed to a fixation treatment.

6. A method according to claim 5, characterized in that the treatment with rotating stencils is applied simultaneously and in registry on opposite sides of the substrate.

7. A method according to claim 5, characterized in that the treatment with rotating stencils is carried out with different kinds of viscous pastes with the understanding that at least one of these must be in the form of a meta-stable foam and must substantially have retained its foam structure after the fixation treatment.

8. A method according to claim 1, characterized in that the substrate has a combined structure of a fibrous web with a network, a woven fabric, or a knitted fabric.

9. A method according to claim 1, characterized in that the substrate has a textile structure.

10. A method according to claim 1, characterized in that the substrate has a foam structure.

11. A method according to claim 1, substantially as described and elucidated in and by the examples.

12. A printed substrate produced using any of claims 1-11.